

INTEGRAL EQUATION THEORY APPLIED TO POLAR MOLECULAR FLUIDS

by

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ABSTRACT

This thesis is an examination of the application of integral equation theory to the study of polar molecular liquids. The integral equation used as the basis for this work is the site-site Ornstein-Zernike (SSOZ) equation coupled with the hypernetted chain (HNC) approximation as the closure. The numerical solution of the SSOZ equation using Gillan's method is examined in detail, and in particular for liquid systems with Coulombic interactions. A method is presented for the symmetry reduction of the Jacobian matrix to facilitate the numerical solution for larger molecular systems. This method is not based on the individual analytic reduction of the matrix integral equation for molecules of particular symmetries, but is a simple procedure within the numerical solution algorithm itself. This allows its general use for molecules of arbitrary symmetry.

It is demonstrated analytically for a non-linear triatomic model with charges on the end sites, that the SSOZ-HNC equation effectively decouples, with the decoupling being dependent on the difference between the multiplicative and additive means of the radial distribution functions involving only charged sites. This decoupling has the consequence that the structural effects due to the dipolar interactions cancel each other out. This results in the dipolar interactions having little or no effect on the calculated structure factor.

The numerical solution to the SSOZ-HNC equation is obtained for a series of hard and soft sphere, non-linear, dipolar, triatomic models. The results obtained show that the dipolar interactions have a very significant effect on the liquid structure but that this is not reflected in the corresponding structure factor due to the effective decoupling of the integral equation.

This effective decoupling phenomenon is predicted to apply to a range of dipolar molecular liquids. To test this, the SSOZ-HNC equation is solved for an interaction site potential model for the highly dipolar, but non-hydrogen bonded liquid, acetonitrile. The radial distribution functions obtained show that the dipolar interactions have a significant effect on the liquid structure.

However, as predicted, there is very little effect on the calculated scattering function. Also, there is very good agreement between the calculated and experimental neutron scattering, coherent differential cross section. Comparison of the SSOZ-HNC radial distribution functions and internal energies with molecular dynamics simulation results from the literature for the same potential showed overall, very good agreement. From these results, it was also concluded that there are two dominant, nearest neighbour orientations in liquid acetonitrile due to the dipolar interactions.